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# **PIXE, Micro-PIXE and RBS Analysis of Thermal Aged Rubber**

## **Material : On The Additives Behaviour Versus Aging Time**

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### **ABSTRACT**

PIXE, micro-PIXE and RBS techniques were employed to monitor the behaviour of additives in industrial formulated rubber material following thermal aging at 152°C in oxidative ambient for a period of time ranging between 0 to 39 weeks. It was found that the rubber loses gradually, with aging time, some of its additives by surface segregation followed by thermal destruction of the segregated species. The comparison of the variation in the relative concentrations of additives with the variation in the mechanical properties as aging time increases can highlight some aspects related to the aging process of the rubber material itself.

**Keywords : PIXE, micro-PIXE, RBS, Rubber, Thermal Aging, Segregation, Additives**

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## 1. INTRODUCTION

Rubber is a highly elastic material composed of long-chain polymer or copolymer materials crosslinked to one another (vulcanization). In order to improve the mechanical and thermal properties of industrial rubber materials, additives are necessary (formulation). The type of rubber and its resulting properties depend on the polymeric structure as well as on the quantities and the composition of various organic and inorganic additives.

In this work, an industrial rubber material based on ethylene/methyl acrylate copolymer, vulcanized and formulated, devoted for specific applications in nuclear environments, was thermally aged at 152°C in oxidative ambient, for a period of time ranging between 0 to 39 weeks. This thermal treatment simulates the more important constraints, on the mechanical properties of the rubber material, observed in normal conditions of use. Mechanical Dynamical Analysis (DMA) demonstrates that there is a constant decrease of elasticity of this material with the thermal aging time [1].

The elasticity loss of this material is directly connected to the modifications of its chemical structure during the aging time. A detailed study on the chemical structure modifications, versus the aging time, demonstrated that the major modifications observed were cross-linking processes via new oxygenated chemical functions produced under the thermooxidation conditions [2]. In fact, the cross-linking process limits the mobility of the polymer chains thus rendering the rubber less and less elastic.

It is known that the elasticity of such material is strongly related to the additives used in the formulation. Waddell and Evans [3] report, using the PIXE technique, a correlation between the concentrations of elements originating from additives and the physical properties of rubber such as break and tear strength.

The knowledge of the behaviour of additives used in the formulation of the studied rubber, under thermal constraint, is very important. This can help in the comprehension of thermal aging processes of the material itself and permits the understanding of some aspects related to changes in the mechanical properties (e.g. elasticity) of the rubber versus thermal aging time.

Thus, in this paper we report on the behaviour of additives of the rubber material versus the thermal aging time using the PIXE, micro-PIXE and RBS techniques. Segregation and thermal degradation processes of additives were highlighted and discussed in relation to elasticity variation of the rubber under thermal treatment.

## **2. EXPERIMENTAL**

### ***2.1 Samples***

The formulation of the rubber was partially known and only few indications about its formulation were given by the fabricant. In fact, lubricants (P-containing aliphatic organic compounds) were added during the realization processes, various mineral additives were used as fillers, black of carbon was used as an antioxydant agent and titanium oxide was used as UV protector. In addition, zinc oxide was used as an activator of the vulcanisation reaction. This reaction, in general, is made using sulfur organic compounds.

8 rubber samples (2 mm thick) were aged in ventilated ovens at 152°C for 0, 2, 6, 10, 13, 19, 27 and 39 weeks. The sample was glued, using double side carbon tape, to the Al sample holder frame (14 mm hole diameter) in order to ensure good electrical contact and the surface that was analysed was the one that was not in contact with the oven. The analysis for each sample was performed at different impact points. The obtained results by PIXE and RBS at the different selected points demonstrate that the samples are practically homogeneous.

## ***2.2 Instrumental set-up and data analysis***

For PIXE measurements, 3 MeV, 1 MeV protons and 1.5 MeV helium beams of  $\sim 3$  mm diameter delivered by the NEC 5SDH 1.7 MV Pelletron tandem accelerator of the Lebanese Atomic Energy Commission were used. The emitted X-rays were detected using a 30 mm<sup>2</sup> active area Si(Li) detector with 170 eV measured FWHM energy resolution at 5.9 keV positioned at 135° referring to the beam direction. A 75  $\mu$ m Kapton® X-rays absorber was inserted between the sample and the detector. In order to have an accurate measurement of the integrated charge during the analysis a secondary electron suppressor biased at  $-400$  V was used. Other details of PIXE measurements are reported in Ref [4].

For RBS measurements the samples were bombarded, under normal incidence, with 2 MeV helium beam. The backscattered particles were detected at 165° using a Canberra SBD with 50 mm<sup>2</sup> active area and 12 keV measured resolution. The Si(Li) and the SBD detectors were connected to a multiparameter system multichannel analyser, allowing simultaneous acquisitions, through conventional electronic chain using standard NIM electronic models.

The X-rays spectra were, in off line mode, analysed with GUPIX computer code [5]. Prior to measurements, operational parameters of the program were determined by measuring a set of thin film standard materials covering an X-ray energy range between 1.5 and 32 keV. Throughout the measurements, the dead time was generally less than 1 % using a beam current of 2 – 20 nA.

Micro-PIXE measurements were performed using the nuclear microprobe facility quadrupole doublet at the Ruder Boskovic Institute [6]. A 3 MeV proton beam, of  $\sim 30$  pA intensity delivered by the EN tandem Van de Graaff accelerator was used. Some selected rubber samples were scanned, on the edges starting from the surface and reaching a  $\sim 1$  mm depth. The X-rays spectra were detected using a Si(Li) detector with  $\sim 175$  eV measured FWHM energy resolution at 5.9 keV positioned at 135° referring to the beam direction.

### 3. RESULTS AND DISCUSSION

#### 3.1 RBS analysis

The RBS is an appropriate technique for the identification of additives, in the range of few microns, by their elemental fingerprints in the rubber material as well as by their depth profiles. Fig.1 shows the RBS spectra of the rubber material for the as received (unaged), the thermally aged for 13 weeks and the thermally aged for 39 weeks samples.

Besides carbon and oxygen, the other detected elements in the RBS spectra can be directly related to the additives used in the formulation of the analysed rubber material. In fact, phosphorus is the fingerprint of the used lubricant while Ca, Si and Na are the fingerprints of other additives, not given by the fabricant, probably used under organometallic and/or mineral forms. The origin of zinc and sulfur is unambiguous since the first is related to the vulcanization reaction activator and the second is used as an organic vulcanisation agent. Carbon and oxygen have more than one origin. Besides the chemical composition of the copolymer itself, the rubber contains ~40% in weight of black of carbon as antioxydant as well as a variety of oxygenated organic and mineral additives. Iron is probably related to impurities of the used antioxydant.

The RBS spectrum of the unaged rubber shows clearly a surface layer containing a variety of additives. From this spectrum it can be observed that: (i) Na and Si are mainly on the surface (ii) the high concentration of oxygen at the surface can be assigned to the segregation of different oxygenated additives, (iii) Ca, Zn and Fe are present mainly at the surface but could have a constant distribution in the analyzed depth and (iv) it is difficult to differentiate S from P; consequently the information on surface or depth distribution for each of those two elements is not possible.

The segregation of additives, already observed in the unaged sample, is enhanced for some of them with the thermal aging time and reaches a maximum after 13 weeks (Fig. 1). In

addition, the formed additives 'surface' layer exhibits a concentration gradient from the surface to the bulk. For an aging time  $> 13$  weeks a degradation process takes place and the surface layer starts to deteriorate gradually. The RBS spectrum of the 39 weeks aging time sample (Fig.1) shows clearly the deterioration of the additives 'surface' layer. From this spectrum one can see that the depth profile of the additives 'surface' layer is so narrow compared to the one observed at 13 weeks. This can indicate that, besides the additives destruction processes, the segregation still exists but with slower kinetics at aging time periods exceeding 13 weeks. In addition, the rubber bulk acts as a reservoir of additives which constantly feeds the surface at different kinetics versus aging time.

As it is observed, the RBS spectra is complicated and the mass resolution limits the characterization of elements with very close  $Z$  values (e.g. P and S). In order to highlight the above processes and to characterize without ambiguities some elements the PIXE technique was used.

### ***3.2 PIXE analysis***

When the analysed depth decreases step by step, by the variation of the nature and/or the energy of the incident projectile, the surface contributes more and more in the X-ray spectrum [4,7]. In this way, information about segregation processes of the different additives can be obtained using the Differential PIXE technique. Fig.2 shows the PIXE spectra of the 13 weeks aging time sample using : (a) 3 MeV protons, (b) 1 MeV protons and (c) 1.5 MeV helium ion beams.

Ca, Fe and Zn had been observed using the RBS technique (see Fig.1). In contrast, other elements which have been hardly differentiated (e.g. P, S and K) or observed (e.g. Ti) by the RBS technique were well identified in the PIXE spectra.

The comparison of PIXE spectra obtained by probing the sample at different depths shows clearly the segregation of additives related to phosphorus and potassium. It is obvious from Fig.2 that with decreasing the analysed depth (using 3 MeV protons to 1.5 MeV helium) the relative intensities of P and K increase. In order to follow the behaviour of the additives surface layer versus the aging time, the rubber samples, thermally aged at different times (0, 2, 6, 10, 13, 19, 27 and 39 weeks), were analysed by PIXE using 1.5 MeV helium beam. Fig.3 shows the variations of the normalized X-rays yields for P, S, K, Ca and Ti versus aging time. The behaviour of elements originating from additive materials as affected by aging time can be discussed via the following points :

1) K, Ca and P have a similar behaviour. Between 0 and 2 weeks the decreasing of the concentrations of these elements in the analysed depth ( $\sim 20 \mu\text{m}$ ) can be easily explained by thermal degradation of the additives surface layer, a process that already exist, in the ‘as received’ rubber material (ie before the thermal aging). The increasing of the P, K and Ca X-ray yields between 2 and 13 weeks indicates that additives segregation process takes place at faster kinetics than the degradation process. In fact, if the kinetics related to thermal degradation of the segregated species can be considered as independant of the thickness of the additives surface layer, the kinetics of the segregation can be highly affected by thermal aging time. This is due to a gradual decrease in the physical affinity between additives and the polymer material resulting from thermal activation constraints. Then the segregation kinetics can be enhanced with increasing the thermal treatment time. The decrease in the physical affinity between additives and polymer material can provoke a separation phase, in the rubber bulk, thus giving rise to heterogeneous additive distributions from the surface to the bulk (see Fig.1-(13 weeks)).

Above 13 weeks the degradation process appears to be the dominant phenomenon. After  $\sim 20$  weeks aging time the X-ray yields reach a quasi stationnary state. This behaviour can be



directly connected to the increasing in the degree of polymer crosslinking which importantly slows the segregation kinetics of the above discussed species. In this way the thermal treatment, for aging times exceeding 13 weeks, acts especially to deteriorate the formed surface additives layer.

Using the DMA technique [1,8,9] it was found that the rubber loses gradually its elasticity with aging time (between 0 and 20 weeks) and the rubber stops evolving to finally reach a quasi non elastic state after ~20 weeks. Besides the crosslinking process, the degradation of the rubber mechanical properties can be related to a gradual loss of additives between 0 and 20, weeks which can favour the crosslinking process (e.g. favours the elasticity loss). After 20 weeks the state of the aged rubber, as mentioned above, limits the loss of additives by segregation and this can be directly related to the observed stationary state of the material starting for 20 weeks aging time.

2) Ti exhibits a reverse behaviour as compared to P, K or Ca. This behaviour reveals that Ti is rather present in the bulk material and is not subjected to segregation processes. This conclusion is supported by the absence of Ti signature from the RBS spectrum which is a relatively surfacique spectrum.

3) For the analysed depth the concentration of sulfur seems to be independent of aging time. It is known that sulfur is used as a vulcanization agent, thus the amount of sulphur in the material is relatively high compared to the other additives. Consequently, additives segregation and/or degradation processes could not significantly affect its concentration in the analysed depth.

4) The PIXE technique clearly shows the segregation of P and indicates that S is not affected by thermal aging of the rubber. These results are very helpful for the interpretation of the RBS spectra. In this way it can be confirmed that the 'surface peak' observed by RBS in the S-P

region is related to phosphorus and that the sulphur is distributed quasi homogenously in the bulk of the material.

### ***3.3 Micro-PIXE analysis***

The additives behaviour was followed at the ‘surface’ of the rubber material (ca 1-2  $\mu\text{m}$ ) using the RBS technique and at the range of 15-20  $\mu\text{m}$  using the PIXE technique (1.5 MeV He beam). The micro-PIXE is the most appropriate technique to monitor the additives behaviour versus thermal aging time at much deeper depth (several hundred microns). This technique can, by probing the edges of some selected samples, give precious information about the segregation and destruction processes already highlighted by the RBS and the PIXE techniques.

Fig.4 shows the distributions of K (0, 2, 13 and 39 weeks aging time) and of S (0 and 39 weeks aging time) obtained by probing the edge of samples from the surface to  $\sim 1\text{mm}$  using 3 MeV proton microbeam. K and S were chosen for their different behaviours in terms of segregation versus aging time; in contrast the very poor statistics obtained for Ti analysis did not permit, in a reasonable acquisition time, the obtention of an accurate distribution.

From these preliminary results it can be shown that: (i) S presents a quasi homogeneous distribution, (ii) for the rubber ‘as received’ (unaged), potassium presents surface segregation with a concentration gradient from the surface to  $\sim 200\ \mu\text{m}$ , (iii) after 2 weeks aging time the potassium ‘surface layer’ disappears while a small concentration gradient still exists between  $\sim 100$  and  $\sim 200\ \mu\text{m}$ , (iii) at 13 weeks aging time the segregation of potassium is enhanced and this layer disappears again for aging time  $> 13$  weeks to obtain a homogeneous depth profile.

These observations are in good agreement with the results obtained by PIXE which have been previously discussed in Fig.3

## CONCLUSION

In this paper, segregation and destruction processes of additives in industrial rubber material thermally aged for periods of time ranging between 0 and 39 weeks at 152 °C under oxidative atmosphere were identified using RBS, PIXE and micro-PIXE techniques.

The thermal segregation of additives was attributed to a decrease in the physical affinity between the additive compounds and the polymer-based rubber material itself.

It turned out that the rubber bulk acts, during the aging process, as an additives reservoir thus feeding the surface at different kinetics. It was demonstrated that before 13 weeks aging time the additives segregation is the dominant process while thermal destruction is the dominant factor above 13 weeks. This is mainly due to an increase in the crosslinking process of the polymer-based rubber material which limits dramatically the segregation process. In addition additives loss, as aging time increases, was suspected to favour the crosslinking process of the bulk.

A possible relationship is noted between the observed evolution of the mechanical properties, such as elasticity, and the behaviour of some additives as the aging time increases.

In this work it was shown that RBS, PIXE and micro-PIXE are complementary and promising techniques that could be applied to study the additives behaviour, at different analysis depths, versus thermal aging time of the rubber material.

## REFERENCES

- [1] P. Dole and J. Chauchard, *Polymer Degradation and Stability*, 56 (1995) 204
- [2] P. Dole and J. Chauchard, *Macromol. Chem. Phys.*, 195, (1994) 3949
- [3] W.H. Waddell and L.R. Evans, *Rub. Plast. News*, May (1994) 23
- [4] B. Nsouli, M. Roumié, K. Zahraman, J.P. Thomas and M. Nasreddine, *Nucl. Instr. and Meth. in Phys. Res. B* (submitted for publication)
- [5] J.A. Maxwell, J.L. Campbell and W.J. Teesdale, *Nucl. Instr. and Meth. in Phys. Res. B* 43 (1989) 218.
- [6] M. Jakšić, L. Kukec and V. Valković, *Nucl. Instr. and Meth. in Phys. Res. B* 77 (1993) 49.
- [7] C. Neelmeijer, I. Brissaud, T. Calligaro, G. Demortier, A. Hautojärvi, M. Mäder, L. Martinot, M. Schreiner, T. Tuurnala and G. Weber, *X-Ray Spectrom.* 29, (2000) 101.
- [8] P. Dole and J. Chauchard, *Die Angew. Makromol. Chem.*, 23 (1996) 79
- [9] P. Dole, Ph.D. Thesis Dissertation (unpublished), Université Lyon I (1995)

## FIGURE CAPTIONS

**Figure 1 :** RBS spectra of the rubber obtained at different aging times: unaged (black line), after 13 weeks aging time (gray line) and after 39 aging time (c-bold black line). The presented spectra were obtained with the same integrated charge (22  $\mu\text{C}$ ).

**Figure 2 :** PIXE spectra of the rubber sample thermally aged during 13 weeks, obtained under: (a) 3 MeV proton beam with an integrated charge of 1 $\mu\text{C}$ , (b) 1 MeV proton beam with an integrated charge of 20 $\mu\text{C}$  and (c) 1.5 MeV helium beam with an integrated charge of 41 $\mu\text{C}$ .

**Figure 3 :** Variations of the X-ray yields (normalized for P at 0 week) versus aging time of Ti, K, Ca, P and S. The experimental points are joint by spline curve and typical error bars are indicated.

**Figure 4 :** Distributions of K and S at different aging time, unaged ( $K_0$ ,  $S_0$ ), for 2 weeks aging time ( $K_2$ ), for 13 weeks aging time ( $K_{13}$ ) and for 39 weeks aging time ( $K_{39}$ ,  $S_{39}$ ). Note that these distributions were obtained at different integrated charge.